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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Method for Selectively Coating Non-Conductors with Carbon Particles and Use of Copper Containing Solutions Therein

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ABSTRACT OF THE DISCLOSURE

A method for coating non-conductors with carbon particles, comprising the following stages: a) treatment with a copper-containing solution; b) coating a non-conductor with an aqueous solution of gelatine or polyacrylate; c) rinsing with water; d) contacting with a dispersion containing carbon, a wetting agent and an ionogenic metal compound; e) rinsing with water. This method selectively produces electrically conducting surfaces, and is suitable for the direct metallization of non-conductors. After being coated with carbon, the non-conductor can be electroplated directly. The use of copper-containing solutions in the method is also described.

METHOD FOR SELECTIVELY COATING NONCONDUCTORS WITH CARBON PARTICLES AND THE USE OF COPPER-CONTAINING SOLUTIONS THEREIN

The invention relates to a method for selectively coating nonconductors with carbon particles and the use of copper-containing solutions therein.

The direct metallization of nonconductors has greatly gained in importance in the last ten years within the printed circuit board industry. In this connection, the direct galvanizing methods with polypyrrole and carbon particles, graphite and/or carbon black should be mentioned.

Direct galvanizing methods by applying carbon particles on nonconductors are described, for example, in the US patents 4,619,741, 4,622,107, 4,622,108, 4,631,117 and 4,684,560. A common and central characteristic within the state of the art is a dipping solution, which contains carbon particles (preferably acidic carbon blacks with particle sizes greater than 3 μm) dispersed in an alkaline surfactant solution. When a nonconductor (substrate) is dipped into such a solution, a film of carbon remains adhered to the surface.

At the same time, relatively thick layers and corresponding amounts of carbon, which afterwards must be removed once again, are deposited, for example, on the copper surface of the printed circuit board.

The copper surface includes not only the external copper lamination of a printed circuit board, but also the drilled inner layers, which are exposed in the case of multilayers and are contacted by the copper sheath deposited later on galvanically.

Large amounts of carbon have a very disadvantageous effect, particularly in the case of fine boreholes, which can become blocked. In addition, excess carbon must be removed from the copper surfaces in a subsequent bath. In order not to remove the carbon from the

nonconductor surfaces, such as epoxide resin, glass, polytetrafluoroethane, polyimide, adhesive and other materials used in the manufacturing of printed circuit boards, a copper etching process is proposed, which takes away up to 5 μm of copper and, at the same time, practically frees the copper surface from carbon. By these means, however, the electrical contact to the carbon lying on the nonconductor is interrupted. In the galvanic bath, the copper layer must first of all bridge the amount of said 5 μm by front growth, in order to contact, for example, an inner layer of a multilayer. However, since the multilayer consists of several layers, 8 to 16 layers being technically customary, there is such a phenomenon at each layer. As a result, there are considerable fluctuations in the thickness of the copper layer in the borehole, which lead to rejects or, at the very least, represent a significant disadvantage of the method. This inadequacy limits the use of this advantageous technique.

A further disadvantage of the methods within the state of the art is the drying process after the coating with carbon particles. In the case of vertical processing techniques, very much of the carbon dispersion remains in the holes here, particularly in holes with a diameter of less than 0.4 mm. Because the surface of the borehole is therefore difficult to dry and because of the unusually thick coating with carbon, further processing is extremely problematical.

It is therefore an object of the invention to make available a selective method, for which there is only a very slight deposition of carbon on the copper surfaces, such as those of a printed circuit board, and for which the adhesion of the carbon particles to the nonconductor surface is increased.

This objective is accomplished owing to the fact that the nonconductor is treated a.) with a copper-containing solution and b.) a polyelectrolyte solution, preferably an aqueous gelatin or polyacrylate solution, is c.) optionally rinsed with water subsequently, and d.) the nonconductor surface is brought into contact with a dispersion containing carbon, wetting agent and an ionogenic metal compound and e.) subsequently optionally rinsed once again with water. Furthermore, the accomplishment of the objective includes the use of copper-containing solutions in the method.

Preferred embodiments are described in the dependent claims.

The inventive method is based on a treatment of a copper surface wherein

1. the copper surface is not covered with carbon particles or covered with carbon particles that adhere only slightly, while the adhesion of the carbon to the nonconductive surfaces, that is, to the surfaces of the glass fibers and of the resin, remains unchanged at a high level and

2. the back-etching of the inner layers is avoided or, at the very least, decreased greatly, because only mild etching solutions are used pursuant to the inventive method.

Pursuant to the invention, this is accomplished furthermore in the following way, owing to the fact that copper compounds are produced on the copper surfaces of the printed circuit board. These copper compounds hamper or make difficult the adsorption of finely-divided carbon or other conductive materials, so that very mild processes subsequently remove these copper compounds and adhering carbon, without etching the copper layer underneath more strongly.

The printed circuit boards, so treated, have an outstanding distribution of layer thicknesses of the galvanic copper in the borehole and, because of the intimate bond between the inner layers and copper hole sheath, withstand thermal processes, such as those required for the soldering shock test at 288°C for 10 seconds.

Surprisingly, it was found that copper(I) compounds, which are formed by the disproportionation reaction of metallic copper with a divalent copper compound, hamper the adsorption of gelatin and carbon.

Compounds of univalent copper, which cannot be obtained directly, are prepared by the exchange reaction of the anions.

As copper compounds, halides, pseudohalides, chalcogenides, sulfates, hydroxides and preferably phosphates come into consideration.

The further step of the inventive method, the treatment of the nonconductor with an aqueous gelatin solution, can be accomplished with solutions, which contain 0.01% to 5.00% and preferably 0.2% of gelatin. All commercial gelatin qualities, which are presently being offered, are suitable for preparing this aqueous gelatin solution. The first step of the method can also be carried out with an aqueous polyacrylate solution instead of a gelatin solution. Here also, all commercially obtainable polymer dispersions based on acrylate or on mixtures, which contain polyacrylate, are suitable.

After this treatment with a gelatin solution or a polyacrylate solution, the nonconductor is rinsed with water, preferably with distilled water.

Subsequently, there is contact between a nonconductor surface, so treated, and a dispersion containing carbon (for example, carbon particles in the form of graphite and/or carbon black), a wetting agent and an ionogenic metal compound (such as an alkali, ammonium or alkaline earth halide).

As wetting agents added, especially phase-transfer catalysts, such as hexadecyltrimethylammonium bromide, are suitable. Furthermore, all phase-transfer catalysts, which contain a quaternary nitrogen atom and are commercially available, are suitable. In addition, Aerosol OT (Cyanamid) and Cathodip® are suitable as wetting agents.

As ionogenic metal compounds, which are to be added to the dispersion, the fluorides, chlorides, bromides or iodides of lithium, sodium, potassium, magnesium, calcium, barium, strontium, ammonium or copper have proven their value.

The coating method is based on the principle of adjusting a carbon dispersion in such a manner, that it is stable in the absence of the substrate that is to be coated. However, if this dispersion comes into contact with the gelatin or polyacrylate layer adhering to the surface of

the nonconductor, this carbon dispersion is destabilized, with the result that there is coagulation and that carbon particles precipitate at the solid/fluorinated phase boundary, adhering firmly. This coagulation is controlled by way of the ionogenic metal compounds (electrolytes) contained in the dispersion.

At the present time, the role of the oligomeric ionophores of the substrate surface cannot yet be defined. However, it is assumed that these lead to a high surface concentration of ions, which is then the cause for the desired coagulation. This coagulation takes place with participation of the oligomeric ionophores, since the coagulation layer is resistant to rinsing.

The inventive method can be used to particular advantage for the direct galvanic metallizing of nonconductors. In this connection, ceramic, glass or other polymeric materials, such as fiber-reinforced plastics containing fillers or plastics that have not been reinforced, epoxides, phenolic resins, cyanate esters, polyether imide, polyimide, fluorine-containing polymers (PTFE) or similar materials can be named as nonconductors. Moreover, it can be used for coating ABS plastic, polyphenyline sulfide, polyesters, polyacrylates and epoxide resins.

The method is also suitable for being used to produce conductor lines or structures on the above-named polymeric materials. Especially emphasized is the treatment of boreholes in printed circuit boards and the use for preparing electromagnetic shielding layers and printed circuit boards.

The inventive method is suitable for use in vertical or horizontal continuous installations, which are operated continuously within industrial galvanic production.

Printed circuit boards, electrodes, heating elements, chip carriers, electronic packages, multichip modules, metallized plastic parts such as buttons, fittings or automobile parts can be produced to advantage with the inventive method.

EXAMPLES

The following Examples are intended to explain the inventive method.

Outline of the Method

1. Cleaning agent; alkaline and acidic
2. Rinsing
3. Treatment in solution A
4. Rinsing
5. Treatment in solution B
6. Rinsing
7. Water-soluble polymer
8. Rinsing
9. Carbon dispersion (graphite/carbon black)
10. Rinsing
11. Removal of the copper(I) compound in a weak etching solution
12. Rinsing
13. Drying with air at 50°C
14. Activating the copper surfaces in an acidic solution
15. Rinsing
16. Galvanic copper 0.5 4 A/dm^2 (depending on the application)

Example 1

A printed circuit board, provided with boreholes, is treated as described above.
Solution A contains 200 g of copper(II) chloride per liter and
Solution B is skipped.

It was possible to clean the board by rinsing it in spray-jet rinsing equipment, so that the exterior copper surfaces and the interior layers were freed from carbon (graphite). After

galvanizing for 5 minutes in the acidic copper electrolyte at 4 A/dm^2, the holes were copper plated tightly.

Example 2

A printed circuit board, provided with boreholes, is treated by the method outlined above.
Solution A contains 200 g of copper(II) chloride per liter and
Solution B contains 50 g of trisodium phosphate per liter.

As in Example 1, the graphite could easily be removed and the galvanizing result was also good.

Example 3

A printed circuit board, provided with boreholes, is treated by the method outlined above.
Solution A contains 200 g of copper chloride per liter and
Solution B contains 50 g of potassium dihydrogen phosphate per liter.

The copper surfaces were free of carbon already after a few seconds of treatment in the weak etching solution (step 11 in the Outline of the Method). After galvanizing for 5 minutes in an acidic copper bath, the holes were copper plated tightly. No free regions could be identified in the transmitted light test.

Example 4

A printed circuit board, provided with boreholes, is treated by the method outlined above.
Solution A contains 50 g of copper(II) bromide per liter and
Solution B contains 50 g of potassium hydrogen phosphate per liter.

After a short time, the copper surfaces were freed from graphite and the copper(I) layer was removed. After 35 μm of copper had been deposited in the center of the borehole, the

multilayer was subjected to a shock test (288°C, 10 seconds) and a polished cross section of it was examined. The contactings were not torn off, the borehole sheath was satisfactory and the layer thickness distribution was 85%, measured from borehole inlet to borehole center.

Example 5

A printed circuit board, pretreated as in Example 3, was treated with a conditioning solution (water-soluble polymer) of 0.2% Mowoiol with a pH of 9 and treated further by the method outlined above. The removal of the carbon also proceeded quickly and the through-plating was free of defects after the given copper-plating time.

Example 6

A printed circuit board, pretreated as in Example 3, was treated with a conditioning solution of 0.2% gelatin with a pH of 9 and then by the method outlined above. The removal of the carbon proceeded rapidly and without problems and the through-plating was without defects after the given copper-plating time.

No defects could be detected in the transmitted light test when the copper layer reached a thickness of 5 μm.

A printed circuit board, reinforced to 35 μm copper, was subjected to a shock test (see above) and found to be satisfactory.

Example 7

The adsorptive coating of nonconducting surfaces with conductive carbon blacks is suitable for the through-plating of printed circuit boards based on glass fiber-reinforced epoxide resin plastics and laminated with copper on both sides.

The board, cleaned in 1% Arkopal® N 150 (Hoechst)/dilute sulfuric acid with ultrasound, is first pretreated for 15 seconds in a 0.2% aqueous gelatin solution with horizontal movement of the goods. For a bath batch, the gelatin, after being allowed to swell for 10 minutes, is first dissolved at an elevated temperature and subsequently allowed to stand for 5 hours at 10°C and then heated to 20°C.

After the board is rinsed with deionized water, it is coated with graphite carbon black of the Sigri company by adsorption from a 1% aqueous dispersion. The dispersing is brought about with ultrasound. The dispersion is stabilized cationically with 2.5 x 10^{-3} moles/L of hexadecyltrimethylammonium bromide (CTAB) and additionally contains 0.07 moles/L of potassium chloride. The coating takes place at a bath temperature of 30°C with horizontal movement of the goods (stroke: 4 cm, frequency: 75 per minute, and is completed in 5 minutes.

The board is washed with deionized water and then dried with compressed air. The thickness of the resulting carbon black layer is less than 1 m and the resistance, based on a square, is of the order of $10^4 \Omega$. To remove the carbon black coating on the copper lamination, the plate is etched anodically for 5 minutes with 1 A/dm in 0.5 moles/L of $CuSO_4/H_2SO_4$ and rinsed once again. After that, it is galvanized in the usual manner.

Example 8

The printed circuit board is coated with carbon black for the through-plating of printed circuit boards as in Example 1. However, the carbon black dispersion is stabilized anionically with Aerosol OT® (Cyanamid). A 1% dispersion of the EC carbon black, Printex® L 6 (Degussa) contains 3.4 x 10^{-13} moles/L of Aerosol OT and 0.04 moles/L of potassium chloride.

Example 9

Printed circuit boards, copper laminated on both sides, are through-plated as in Example 1, here, however, by way of a coating with graphite. The aqueous graphite dispersion used (with

a particle size of 0.4 to 0.6 μm) is a product of the Acheson company with the name of "Aquadag®" and is used in a dilution of 1 : 6. The coating is carried out for 5 minutes with a horizontal movement of the goods (stroke: 4 cm, frequency: 50 per minutes) at a bath temperature of 25°C. Despite the fact that the resistance of the graphite coating (approximately $10^6\Omega$/square) is significantly higher than that of carbon black layers, the galvanic deposition of copper proceeds better on graphite.

Example 10

The board is through-plated over a coating with graphite, as in Example 3. The coating is achieved, however, after a pretreatment of the printed circuit board by immersion in Basoplast® 280 D (BASF). Basoplast 280 is a cationically stabilized, aqueous polymer dispersion based on acrylate, which is usec a dilution of 1 : 5. The immersion takes place during a 15 second lifting motion at room temperature. The board is rinsed with deionized water and then coated with graphite. Compared to the pretreatment with gelatin, the coating admittedly is less, with a resistance of approximately $10^7\Omega$/square. Nevertheless, the board can be galvanized without difficulties.

Example 11

Because they are coated repeatedly with graphite, the epoxide resin boards can be galvanized flat. As in Example 3, the epoxide board (2 cm wide, 2 cm high) is immersed in gelatin solution and rinsed and then coated with graphite for a period of, however, 2 minutes. After being rinsed, the coated board is immersed once again in gelatin solution, rinsed and coated with graphite in the same way for a second time. This type of coating is repeated twice more, after which the board is dried with compressed air.

During the galvanizing, the contacting to the graphite layer is also immersed in the bath. Starting with the contacting, the copper deposited spreads over the graphite layer.

Example 12

As in Example 5, glass can also be galvanized flat. Moreover, the workpieces can have any shape. The adhesion of the metallization to glass is, however, less than that of the metallization to epoxide resin.

Example 13

A preheated glass plate (2 cm wide, 2 cm high) is exposed at room temperature for 5 minutes to gaseous hydrofluoric acid in a closed container. During this time the surface is roughed uniformly. After the reaction products are rinsed from it, the plate is metallized as described in Example 5. The adhesion of the galvanic coating is clearly better than that of a galvanic coating on an untreated glass plate.

Example 14

An epoxide or glass plate is coated with graphite as described in Examples 5 to 8. After the last rinsing, however, the plates are dried in an oven for 15 minutes and tempered. For epoxide boards the temperature is 120°C and for glass plates 200°C. The conductivity of the graphite layers is increased by this treatment, so that the galvanic deposition of copper proceeds more quickly. By these means, it is also possible to galvanize larger workpieces, particularly of glass.

Example 15

A glass plate (2 cm high, 2 cm wide) is coated with a polymer. As polymer, the binder of the BASF electrophoretic enamel "Cathodip®", which is a water-dilutable dispersion (product number FT 83-0270), is used as polymer. The dispersion is applied by immersing the plate in the 1 : 1 diluted polymer dispersion and subsequently drying for 5 minutes at 80°C. The transparent, adhering layer is water resistant and shows hydrophobic behavior. Thereupon, the procedure of Example 5 is followed and, after the graphite coating, copper is deposited

galvanically. The metallization on this surface shows a better adhesion strength than the metallization on glass that has not been coated with polymer. A further increase in adhesion is achieved due to the cross linking of the polymer after the galvanization. It takes place while stoving at a temperature of 180°C for a period of 15 minutes.

Example 16

A glass plate, 2 cm high, 2 cm wide, is coated with a water-insoluble gelatin layer from a 0.5% gelatin solution, which contains 0.5% formaldehyde, by briefly immersing the plate in the solution at a temperature of 20°C and subsequently drying it with compressed air. Without any further pretreatment, the plate is coated with graphite by adsorption from the dispersion used in Example 3 at a temperature of 25°C for 2 minutes with movement of the plates. The plates are then rinsed and dried with compressed air. After that, the plates are dipped for a second time, again for 2 minutes, into the graphite dispersion and dried once more. This procedure is repeated twice more. Subsequently the plates are copper plated galvanically in the usual manner.

Example 17

The through-plating of a printed circuit board, copper laminated on both sides, is achieved over a coating with graphite. For this purpose, the graphite dispersion described in Example 3 is used, however at a dilution of 1 : 4. Furthermore, Arkopon® T Pk, a Hoechst anionic surfactant, is added at a concentration of 70 ppm.

The board, cleaned as described in Example 1, is coated by being immersed briefly, freeing the boreholes by blowing compressed air through them and drying for 5 minutes at 80°C. The boards are etched as in Example 1 and subsequently copper plated galvanically.

Example 18

Through-Plating Printed Circuit Boards: An epoxide resin multilayer with boreholes less than 1 mm in diameter is cleaned in an aqueous solution, which contains 0.5% Arkopal N150 (HOECHST) and 5% sulfuric acid. The cleaning requires 2 minutes, ultrasound being used at the same time.

After being rinsed for 30 seconds with tap water, the board is immersed for 1 minute in an aqueous solution, which contains 100 g/L of sodium peroxodisulfate and 20 g/L of sulfuric acid, and rinsed once again. Subsequently, the board is treated for 1 minute in a hydrochloric acid solution of 200 g/L copper chloride (pH of 1.8) at a temperature of 40°C. After being rinsed with tap water, the board is immersed in a gelatin solution, rinsed once again and then coated with carbon black as in Example 1, however for a period of 2 minutes.

The board is rinsed and subsequently immersed for 2 minutes at room temperature in an aqueous solution, which contains 50 g/L of sodium peroxodisulfate and 50 g/L of sulfuric acid. After being rinsed with a strong jet, the board is dried with hot air at 110°C.

Finally, the board is copper plated electrolytically in Cupracid GS (Schering) at room temperature with a current density of 4 A/dm^2 for a period of 40 minutes.

Example 19

Through-Plating Printed Circuit Boards: A polyimide multilayer (Starr-Flex), which is provided with boreholes having a diameter of less than 1 mm, is cleaned as in Example 18. After being rinsed for 30 seconds with tap water, the board is immersed at room temperature for 1 minute in an aqueous solution, which contains 100 g/L of sodium peroxodisulfate and 20 g/L of sulfuric acid and rinsed once more. Subsequently, the board is treated for 1 minute in a hydrochloric acid solution of 200 g/L of copper chloride (pH of 1.8) at a temperature of 40°C and after being rinsed once more, treated in a 10% solution of potassium dihydrogen phosphate, also at 40°.

After being rinsed with tap water, the board is immersed in a gelatin solution as in Example 18, rinsed once more and then coated with graphite as in Example 17, however for a period of 2 minutes.

The board is rinsed and subsequently immersed for 1 minute at room temperature in an aqueous solution, which contains 50 g/L of sodium peroxodisulfate and 50 g/L of sulfuric acid. After being rinsed with a powerful stream, the board is dried with hot air at 110°C. Subsequently, the board is copper plated electrolytically as in Example 18.

Claims

1. A method for selectively coating nonconductors with carbon particles, wherein a substrate is subjected to the following steps:

   a. treatment with a copper-containing solution,

   b. coating the nonconductor with a 0.01% to 5.00% aqueous solution of gelatin or polyacrylate,

   c. optionally rinsing with water,

   d. contacting with a dispersion containing carbon, wetting agent and an ionogenic metal compound, and

   e. cptionally rinsing with water.

2. The method for coating nonconductors with carbon particles of claim 1, wherein graphite and/or carbon black are/is used as carbon particles.

3. The method for coating nonconductors with carbon particles of claim 1, wherein anionic or cationic surfactants or phase-transfer catalysts are used as wetting agents.

4. The method for coating nonconductors with carbon particles of claim 1, wherein a copper(I) solution and/or a copper(II) solution are/is used as copper containing solution.

5. The method of claim 4, characterized in that the copper(I)-containing solution contains carbonate, chloride, chromate, citrate, hydroxide, bromide, iodide, sulfate, sulfide, phosphate or thiocyanate as anion or mixtures of anions.

6. The method of claim 4, characterized in that the concentration of copper is 0.5 to 100.0 g/L.

7. The method of claim 4, characterized in that the pH of the copper solution lies in the acidic range, preferably between 1 and 4.

8. The method for coating nonconductors with carbon particles of claim 1, wherein fluorides, chlorides, bromides or iodides of lithium, sodium, potassium, magnesium, calcium, barium, strontium, ammonium or copper are used as ionogenic metal compounds.

9. The method of claims 1 and 2, characterized in that graphite with an average particle diameter of less than 50 μm and/or carbon black with an average particle diameter of less than 5μm are/is used as carbon particles.

10. The use of the method of at least one of the claims 1 to 12 for coating, particularly for the direct, galvanic metallization of polymers, ceramic or glass.

11. Use of the method of at least one of the claims 1 to 12 for producing conductor lines or structures on polymer materials.

12. Use of the method of at least one of the claims 1 to 12 for the direct, galvanic metallization of boreholes of printed circuit boards.

13. The use of the method of at least one of the claims 1 to 12 for producing printed circuit boards.

14. The use of the method of at least one of the claims 1 to 12 in horizontal, continuously operated installations.

15. The use of a copper(I)- and/or copper(II)-containing solution for the pretreatment of nonconductors before they are treated with carbon particles.